

Composite elements comprising (i) thermoplastic polyurethanes and (ii) microcellular polyurethane elastomers

5 The invention relates to composite elements comprising

(i) thermoplastic polyurethanes, also referred to below as TPUs, and, adhering thereto,

10 (ii) microcellular polyurethane elastomers with a density of from 300 to 700 kg/m<sup>3</sup>, a tensile strength to DIN 53571 of from 3 to 8 N/mm<sup>2</sup>, an elongation at break to DIN 53571 of from 350 to 550%, a tear propagation resistance to DIN 53515 of from 8 to 30 N/mm and a rebound resilience to DIN 53512 of from 50  
15 to 60%.

The invention further relates to a process for producing these composite elements, and to their use.

20 Composite elements based on metals and rubber, also generally known as rubber-metal composites, are well known. They are widely used, for example in the running gear of road vehicles, and are described, for example, in "Fahrwerktechnik: Radaufhängungen", 2nd edition, ed. Prof. Dipl.-Ing. Jörnßen Reimpell, Vogel  
25 Buchverlag Würzburg, in particular on pages 77, 83, 84, 87, 281, 286 and 290. Disadvantages of these composites are the high density of their metal constituents, the relatively short service life of the rubber, and also loss of adhesion between the rigid and flexible elements of the component. It is known that this can  
30 be improved by using adhesion promoters, which are applied as liquids to the rigid elements and solidify and, where appropriate, have to be reactivated by heating. These procedures for application and reactivation are time-consuming and costly and should therefore be avoided.

35 It is well known that microcellular polyurethane elastomers can be used as a flexible element replacing the rubber. DE-A 195 48 771 and 195 48 770 describe polyurethane elastomers of this type and their use as damping elements.

40 It is an object of the present invention to develop composite elements which can serve as replacement for known rubber-metal composites, in particular reducing the weight of the composites. In addition, the adhesion between the components of the composite  
45 elements should be improved and, in particular, the use, described above, of adhesion promoters avoided.

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We have found that this object is achieved by means of the composite elements defined at the outset.

The composite elements may preferably be produced by preparing  
5 (ii) in the presence of (i), basing (i) on the reaction of (a) isocyanates with (b) compounds reactive to isocyanates, if desired in the presence of (d) catalysts and/or (e) auxiliaries and/or additives, where the ratio of the isocyanate groups present in (a) to the groups present in (b) and reactive to  
10 isocyanates is preferably greater than 1.06:1, particularly preferably from 1.1 : 1 to 1.2 : 1.

In the reaction mixture to prepare the TPU (i), isocyanate groups are preferably present in excess over the groups reactive to  
15 isocyanate groups. This excess can be expressed in terms of the molar ratio of the isocyanate groups in component (a) to the groups in component (b) which are reactive to isocyanates. As described, this ratio is preferably greater than 1.06 : 1, particularly preferably from 1.1 : 1 to 1.2 : 1.

20 Due to this excess of isocyanate groups, the free isocyanate groups react with the starting components for the microcellular polyurethane elastomers when these are prepared, in particular with components (b) in the preparation of (ii), giving markedly  
25 improved bonding and thus adhesion between (i) and (ii). During and in some cases after the formation of the urethane groups by the reaction of (a) with (b) the free isocyanate groups can also create internal crosslinking in the TPU (i) in the form of, for example, allophanate and/or isocyanurate structures which lead to  
30 the improved properties of the TPU. If desired, the creation of the crosslinking may be promoted by adding catalysts, e.g. alkali metal acetates or formates, which are well known for this purpose. The processing of the reaction product, i.e. the TPU, to give films, moldings, injection-molded items, tubing, cable  
35 sheathing and/or fibers should preferably take place during and/or directly after the creation of the urethane groups and prior to complete reaction of the reaction mixture, since preference is given to thermoplastic processing of the polyisocyanate polyaddition products to give films, moldings or  
40 fibers at low temperatures prior to and/or during the development of crosslinking.

The reaction of the starting components in the process for preparing TPU (i) may take place by known processes, for example  
45 the one-shot process or the prepolymer process, for example by reacting an NCO-containing prepolymer prepared from (a) and some of components (b) with the remainder of (b) on a conventional

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belt system, or using a known reactive extruder or systems known for this purpose. The temperature for this reaction is usually from 60 to 250°C, preferably from 60 to 180°C, particularly preferably from 70 to 120°C. During and, where appropriate, after  
5 the creation of the urethane groups by reacting (a) with (b) the reaction products may be pelletized or granulated or processed by well known methods, for example by extrusion in known extruders, by injection molding in conventional injection-molding machines or by well known spinning processes, for example by melt  
10 spinning, to give any type of molding or in particular a film.

The reaction mixture for preparing the TPU (i) will preferably be processed in extruders or injection-molding machines to give films or moldings, or by the spinning process to give fibers,  
15 during and, in some cases, after the creation of the urethane groups by reacting (a) with (b), particularly preferably from the reaction melt and prior to fully developed formation of allophanate and/or isocyanurate crosslinking. This direct further processing of the reaction mixture without granulation or  
20 pelletization and without substantial or complete reaction of the reaction mixture has the advantage that there has been very little or no crosslinking by the creation of, for example, allophanate structures and/or isocyanurate structures, and the reaction mixture can therefore be processed at a desirably low  
25 temperature to give the final products, such as films or moldings.

A preferred method of processing the reaction mixture is therefore to process the reaction mixture for preparing the TPU  
30 (i) in a softened or melted state during the reaction of (a) with (b), particularly preferably from the reaction melt and prior to fully developed formation of an allophanate and/or isocyanurate crosslinking, at from 60 to 180°C, preferably from 70 to 120°C, in extruders or injection-molding machines, to give films or  
35 moldings.

The product of the process, i.e. the TPU from the extruder or injection-molding machine may preferably be annealed at from 20 to 120°C, preferably from 80 to 120°C for from 2 to 72 hours under  
40 the conditions which are otherwise usual. If unsaturated components (b) are used for preparing the TPU, for example cis-1,4-butenediol, the moldings or films may be treated by irradiation, such as electron-beam irradiation, after they have been produced.

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According to the invention, the TPUs (i) obtainable in this way are used for producing the composite elements. The TPUs (i) are particularly preferably used in the form of moldings, usually with a thickness of from 2 to 12 mm.

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According to the invention, the composite elements are produced by preparing the microcellular polyurethane elastomers in the presence of (i). Microcellular polyurethane elastomers (ii) and processes for their preparation are well known. They preferably have a density of from 300 to 700 kg/m<sup>3</sup>, preferably from 350 to 650 kg/m<sup>3</sup>, a tensile strength to DIN 53571 of from 3 to 8 N/mm<sup>2</sup>, preferably from 3.0 to 7.0 N/mm<sup>2</sup>, an elongation at break to DIN 53571 of from 350 to 550%, preferably from 350 to 400%, a tear propagation resistance to DIN 53515 of from 8 to 30 N/mm,

**15** preferably from 8 to 20 N/mm, and a rebound resilience to DIN 53512 of from 50 to 60%, and particularly preferably a cell size of from 50 to 500  $\mu\text{m}$ .

(ii) may be prepared by the well known reaction of (a)

20 isocyanates with (b) compounds reactive to isocyanates, in the presence of (c) blowing agents and, if desired, (d) catalysts and/or auxiliaries and/or additives (e).

(ii) is preferably prepared in the presence of (i) in such a way

25 that the surface of (i) is degreased, for example using  
conventional, preferably organic, solvents, and then (a)  
isocyanates are reacted with (b) compounds reactive to  
isocyanates, in the presence of (c) blowing agents and, if  
desired, (d) catalysts and/or (e) auxiliaries and/or additives in  
30 order to prepare (ii) in the presence of (i).

The amounts of (a) and (b) reacted to prepare (ii) are preferably such as to give a ratio of equivalents of NCO groups in the polyisocyanates (a) to the total of the reactive hydrogen atoms

**35** in components (b) of 0.8 : 1 to 1.2 : 1.

The microcellular polyurethane elastomers (ii), and therefore the novel composite elements, are advantageously produced by the one-shot process or prepolymer process, for example using the

40 high-pressure or low-pressure technique in open or closed, preferably closed, molds, such as metallic molds, or free-foamed (in-situ foam). The composite elements are preferably produced in molds into which the TPU (i) is preferably placed in the form of a molding. The reaction of the starting components for preparing 45 (ii) takes place in direct contact with (i), so that the reaction of the starting components produces a bond between (i) and (ii). The internal walls of the molds, in particular those which come

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into contact with the starting components for preparing (ii), may preferably be provided with a conventional mold-release agent.

(ii) is particularly preferably prepared in a closed mold, preferably with a degree of compaction of from 1.1 to 8,

5 particularly preferably from 2 to 6.

The starting components are usually mixed at from 15 to 90°C, preferably from 20 to 60°C and in particular from 25 to 45°C, and introduced into the open or closed mold. The temperature of the

10 internal surface of the mold is usefully from 20 to 110°C, preferably from 30 to 100°C and in particular from 70 to 90°C.

In a prepolymer process prepolymers having isocyanate groups are preferably used. The prepolymers preferably have isocyanate

15 contents of from 3 to 5% by weight, based on the total weight.

These may be prepared by well known processes, for example by reacting a mixture which comprises an isocyanate (a) and at least one compound (b) reactive to isocyanates, the reaction usually taking place at from 80 to 160°C, preferably from 90 to 150°C. If

20 the prepolymer to be prepared has isocyanate groups an appropriate excess of isocyanate groups over the groups reactive to isocyanate is used in the preparation. The reaction generally ends after from 15 to 200 min.

25 A preferred method for the process is to prepare (ii) in a closed mold in contact with (i) by reacting a prepolymer having isocyanate groups with a crosslinking agent component comprising (c) blowing agent, (d) catalysts and (e) auxiliaries and/or additives. The crosslinking agent component preferably comprises

30 (c) water, (d) catalyst and, as (e), polysiloxanes, such as polyethermethysiloxanes, sulfated castor oil or n-alkylbenzenesulfonic acids having from 9 to 15 carbon atoms in the alkyl radical.

35 Examples of components (a) to (e) will be given below. Unless otherwise stated, the unit of the molar masses given below is g/mol.

a) Well known isocyanates (a) which may be used are in particular organic isocyanates, for example aliphatic, cycloaliphatic, araliphatic and/or aromatic isocyanates, preferably diisocyanates. Individual examples are:

40 hexamethylene 1,6-diisocyanate, 2-methylpentamethylene 1,5-diisocyanate, 2-ethyl-1,4-butylene diisocyanate, pentamethylene 1,5-diisocyanate, butylene 1,4-diisocyanate,

45 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (isophorone diisocyanate, IPDI), cyclohexane

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- 1,4-diisocyanate, 1-methylcyclohexane 2,4- and/or  
-2,6-diisocyanate, dicyclohexylmethane 4,4'-, 2,4'- and/or  
2,2'-diisocyanate, 1,4- and/or  
1,3-di(isocyanatomethyl)cyclohexane, 1,4- and/or  
5 1,3-di(isocyanatoethyl)cyclohexane, 1,3- and/or  
1,4-di(isocyanatomethyl)benzene, tolylene 2,4- and/or  
2,6-diisocyanate (TDI), p-phenylene diisocyanate (PDI),  
p-cyclohexane diisocyanate (CHDI), 3,3'-dimethylbiphenyl  
4,4'-diisocyanate (TODI), diphenylmethane 4,4'-, 2,4'- and/or  
10 2,2'-diisocyanate (MDI), mixtures of diphenylmethane 2,4'-  
and 4,4'-diisocyanate, urethane-modified liquid  
diphenylmethane 4,4'- and/or 2,4'-diisocyanates,  
4,4'-diisocyanato-1,2-diphenylethane and/or naphthylene  
1,5-diisocyanate (NDI). Preference is given to the use of  
15 hexamethylene 1,6-diisocyanate, IPDI, MDI and/or TDI for  
preparing the TPU. The microcellular polyurethane elastomers  
are preferably based on MDI, PDI, CHDI, TODI and/or NDI,  
particularly preferably MDI and/or NDI.
- 20 b) The substances (b) used for preparing the TPU (i) and  
reactive to isocyanates preferably comprise compounds (b1)  
which are reactive to isocyanates and have molar masses of  
from 500 to 8000, preferably those whose average  
functionality, i.e. functionality averaged over component  
25 (b), is from 1.8 to 2.5, preferably from 1.9 to 2.2,  
particularly preferably from 1.95 to 2.1. Suitable examples  
are polyhydroxy compounds, preferably polyetherols and  
polyesterols.
- 30 The mixtures for preparing the TPUs and, respectively, the  
TPUs must be at least predominantly based on difunctional  
substances reactive to isocyanates.
- 35 Other compounds which may be used as substances (b) reactive  
to isocyanates are polyamines, for example amine-terminated  
polyethers, e.g. the compounds known as Jeffamine® (Texaco  
Chemical Co.), and the average functionality of component (b)  
should lie within the specified range.
- 40 Preference is given to the use of polyetherols based on  
conventional starter substances propylene 1,2-oxide and ethylene  
oxide, and in which more than 50%, preferably from 60 to 80%, of  
the OH groups are primary hydroxyl groups and in which at least  
some of the ethylene oxide has been arranged as a terminal block,  
45 and in particular polyoxytetramethylene glycols.

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The polyetherols, which in the case of the TPUS are essentially linear, usually have molar masses of from 500 to 8000, preferably from 600 to 6000 and in particular from 800 to 3500. They may be used either individually or as mixtures with one another.

- 5 Suitable polyesterols may be prepared, for example, from dicarboxylic acids having from 2 to 12 carbon atoms, preferably from 4 to 8 carbon atoms, preferably adipic acid and/or aromatic dicarboxylic acids, such as phthalic acid, isophthalic acid and/or terephthalic acid, and di- or polyhydric alcohols, such as ethanediol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,10-decanediol, 2,2-dimethyl-1,3-propanediol, 1,2-propanediol, diethylene glycol and/or dipropylene glycol.
- 10 The polyesterols usually have molar masses of from 500 to 6000, preferably from 800 to 3500.

Component (b) may also comprise other well known chain extenders (b2), which usually have molar masses of less than 500 g/mol, preferably from 60 to 499 g/mol, particularly preferably from 60 to 300 g/mol, in addition to the compounds (b1) mentioned. Examples of these are alkanediols and/or alkenediols and/or alkynediols having from 2 to 12 carbon atoms, preferably having from 2, 3, 4 or 6 carbon atoms, for example ethanediol, 1,6-hexanediol and in particular 1,4-butanediol and/or cis- and/or trans-1,4-butanediol, 1,3-propanediol, 1,2-propanediol and/or diethylene glycol, for example ethanediol, diethylene glycol and dipropylene glycol. Other suitable compounds are diesters of terephthalic acid with alkanediols having from 2 to 4 carbon atoms, e.g. the bis(ethanediol) or bis(1,4-butanediol) ester of terephthalic acid and/or diethylene glycol and dipropylene glycol.

- 25 1,2-propanediol, 1,3-propanediol, 1,4-butanediol and/or diethylene glycol and/or diethylene glycol and/or dipropylene glycol. Other suitable compounds are diesters of terephthalic acid with alkanediols having from 2 to 4 carbon atoms, e.g. the bis(ethanediol) or bis(1,4-butanediol) ester of terephthalic acid and/or diethylene glycol and dipropylene glycol.
- 30 bis(1,4-butanediol) ester of terephthalic acid and/or diethylene glycol and dipropylene glycol. Other suitable compounds are diesters of terephthalic acid with alkanediols having from 2 to 4 carbon atoms, e.g. the bis(ethanediol) or bis(1,4-butanediol) ester of terephthalic acid and/or diethylene glycol and dipropylene glycol.
- 35 (b2) may be varied within a relatively wide range. Molar ratios which have proven successful are (b1) : (b2) = from 1 : 1 to 1 : 12, in particular from 1 : 1.8 to 1 : 6.4, where the hardness and melting point of the TPUS rise with increasing (b2) content.

- 40 Component (b1) in component (b) for preparing the microcellular polyurethane elastomers (ii) may comprise, in addition to the components (b1) mentioned, well known compounds reactive to isocyanates, for example polyetherols and/or polyesterols with a molar mass of from 500 to 8000 and with functionality of from 1.8 to 5. In addition to the chain extenders previously mentioned as (b2) for (ii) use may be made of well known crosslinking agents (b3) which usually have a functionality of from 3 to 6 and a

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molar mass of less than 500, preferably from 30 to 400. (b) for preparing (ii) preferably comprises polyesterols with a functionality of from 2 to 3 and a molar mass of from 50 to 8000.

- 5 c) Blowing agents (c) which can be used for preparing the microcellular polyurethane elastomers (ii) preferably include water, which reacts with isocyanate groups to form carbon dioxide. The amounts of water usefully used are from 0.1 to 8 parts by weight, preferably from 0.3 to 3.0 parts by weight, 10 in particular from 0.3 to 2.0 parts by weight, based on 100 parts by weight of component (b).

If desired, known physical blowing agents may also be used in a mixture with water. Water is particularly preferably used 15 as sole blowing agent.

- d) Suitable catalysts which in particular accelerate the reaction between the NCO groups in the diisocyanates (a) and the hydroxyl groups in structural components (b), are those 20 known from the prior art, for example the conventional tertiary amines, e.g. triethylamine, dimethylcyclohexylamine, N-methylmorpholine, N,N'-dimethylpiperazine, 2-(dimethylaminomethoxy)ethanol, diazabicyclo[2.2.2]octane, and also in particular organometallic compounds, such as 25 titanate esters, iron compounds, e.g. iron(III) acetylacetonate, tin compounds, e.g. tin diacetate, tin dioctoate, tin dilaurate or the dialkyltin salts of aliphatic carboxylic acids, for example dibutyltin diacetate or dibutyltin dilaurate. The amounts usually used of the 30 catalyst (c) are from 0.002 to 0.1 parts per 100 parts of (b).

- e) Examples of conventional auxiliaries and/or additives (d) which may be used are surface-active substances, flame 35 retardants, nucleating agents, oxidation inhibitors, stabilizers, lubricants, mold-release agents, dyes and pigments, inhibitors, stabilizers counteracting hydrolysis, reaction of light or heat, or discoloration, inorganic and/or organic fillers, reinforcing agents and plasticizers. Other 40 particular auxiliaries and/or additives for preparing (ii) are those mentioned in lines 6 to 16 on page 8 of DE-A 195 48 771, for example the abovementioned polysiloxanes, such as polyethermethoxysiloxanes, sulfated castor oil and n-alkylbenzenesulfonic acids having from 9 to 15 carbon atoms 45 in the alkyl radical.



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Further details concerning the abovementioned auxiliaries and additives can be found in the technical literature.

The novel composite elements are preferably used as damping  
5 elements in motor vehicle construction, for example in automotive construction as transverse link bearings, rear-axle subframe bearings, stabilizer bearings, longitudinal link bearings, spring-strut support bearings, shock-absorber bearings and/or bearings for triangular links.

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The novel composite elements, in particular the damping elements, have not only markedly improved adhesion between the thermoplastic polyurethanes (TPUs) (i) and the microcellular polyurethane elastomers (ii) but also improved mechanical  
15 properties of (i), in particular in relation to abrasion and tensile strength.

These advantages will be demonstrated using the examples below.

## 20 Preparation of the TPU (i)

The mixes described in Table 1 were reacted in a reactive extruder using the parameters given in Table 2 to give thermoplastic polyurethanes. This TPU was then used to produce  
25 test specimens of dimensions 120 mm x 30 mm x 5 mm. The properties of the TPUs and, respectively, of the test specimens are given in Table 2.

Table 1

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Component A	Amount [parts by weight]
Polyol 1	51.54
1,4-Butanediol	10.93
Elastostab® H01	0.41
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Component B:	
Lupranat® MET	Proportion given by key number

40 Polyol 1: Lupraphen® 9066, commercially available from Elastogran GmbH

Elastostab® H01: hydrolysis stabilizer from Elastogran GmbH

Lupranat® MET: isocyanate commercially available from Elastogran  
45 GmbH

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Table 2

Example		1	2	3	4
Key number		100	105	110	115
5	Total isocyanate content in TPU, unannealed [%]	0.30	0.48	0.47	0.47
	Total isocyanate content in TPU, annealed for 30 min at 120°C [%]	0.18	0.47	0.47	0.47
	Elongation at break [%]	490	480	490	480
	Tensile strength [N/mm <sup>2</sup> ]	53	55	54	56
10	Abrasion [mm <sup>3</sup> ]	25	30	40	37
	Shore hardness [D]	55	54	57	57
	Density [g/cm <sup>3</sup> ]	1.21	1.21	1.215	1.215

- The method of producing the composite elements was to place the
- 15 cleaned specimens individually into a mold and introduce a reaction mixture into the mold. The microcellular polyurethane was produced in direct contact with the TPU. The mold temperature was 60°C.
- 20 The reaction mixture used to prepare the microcellular polyurethanes was a system as set out in Kunststoffhandbuch, Vol. 7, "Polyurethane", ed. Günter Oertel, 3rd edn., 1993, Carl-Hanser-Verlag, page 428, Example 5.
- 25 The composite elements produced had densities of 600 g/cm<sup>3</sup>. They were then annealed for 16 hours at 110°C, and their properties were tested after a further 5 to 21 days. In particular, the ultimate tensile strength of the composite elements and the nature of their fracture were tested. The advance rate in the
- 30 tensile test was 20 mm/min. The composite elements consisting of two TPU specimens which had been adhesive-bonded by microcellular polyurethane were clamped into the machine via the TPUs in such a way that they could be subjected to tensile and shear stresses until they fractured. For this the TPU specimens were pulled in
- 35 opposite directions at the stated advance rate. Table 3 gives the properties of the composite elements.

Table 3

40	TPU	Ultimate tensile strength [N/mm <sup>2</sup> ]	Nature of fracture
	Example 1 (Key number 100)	1.07	PU separated from TPU, small residues of PU on the TPU
45	Example 2 (Key number 105)	1.23	PU separated from TPU, residues of PU on the TPU

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Example 3 (key number 110)	1.51	Some separation of PU from TPU, residues of PU on the TPU
Example 4 (key number 115)	1.52	Some separation of PU from TPU, residues of PU on the TPU

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The abbreviation PU in Table 3 indicates the microcellular polyurethanes. As the key number of the TPU rises, the ultimate tensile strength of the composite made from TPU and microcellular polyurethane increases.

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The results show that the object has been achieved by means of the novel composite elements. The novel composite elements have markedly improved ultimate tensile strength. In addition, the nature of the fracture indicates that the adhesion between the cellular polyurethanes and the TPU has been significantly improved.

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